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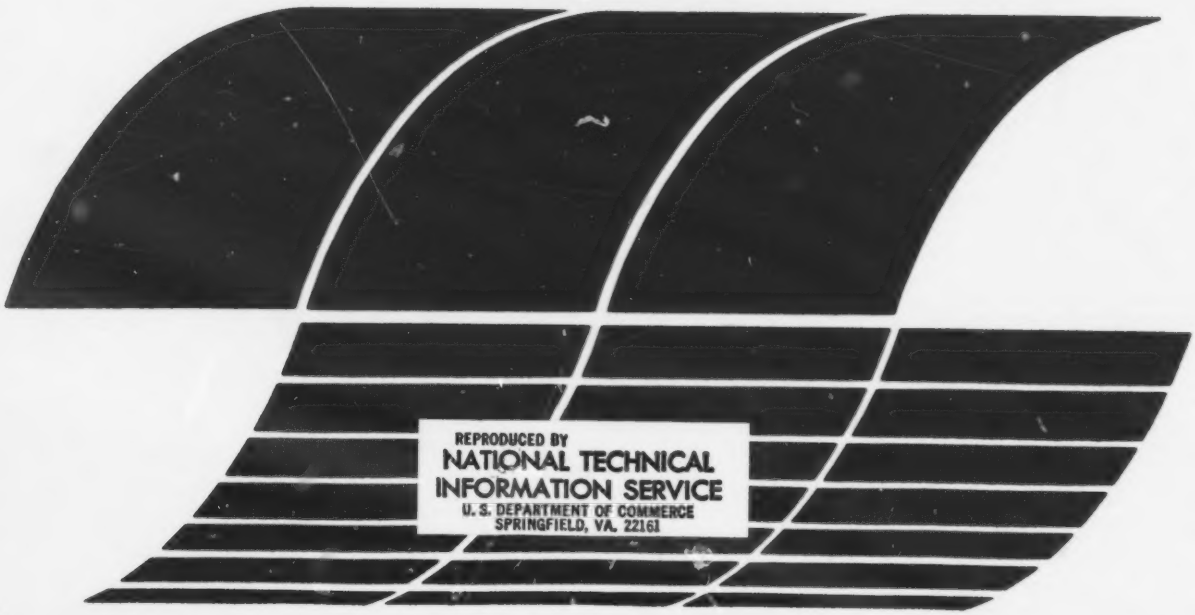

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Coal Sulfur Measurements

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ABSTRACT

A new technique for sulfur forms analysis based on low temperature oxygen plasma ashing has been developed. In this method the low temperature plasma ash is analyzed by modified ASTM techniques after the organic material has been selectively removed. The proposed procedure has been tested on 25 coals and compared with ASTM analyses with excellent results. The data indicate that it is significantly more accurate and precise than ASTM D2492. A separate set of experiments has shown that it is also feasible to determine organic sulfur directly by trapping SO_x in the plasma ash effluent. Development of the latter procedure was beyond the scope of the task.

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1. CONCLUSIONS

A new technique for sulfur forms analysis has been developed in response to a long-term need by the coal cleaning community for a more accurate and precise procedure. In this method, low temperature oxygen plasma ashing is used to selectively remove the organic matrix so that inorganic sulfur can be extracted and analyzed without interferences associated with the organic matrix. The inorganic sulfur can be analyzed for sulfur forms by a modified ASTM technique or total inorganic sulfur by a highly accurate $BaSO_4$ gravimetric procedure. Specific findings are listed below.

- Plasma ashing is greater than 99% specific to the organic matrix as shown by separate oxidation studies on FeS_2(pyrite), FeS, PbS, and ZnS. The converted sulfide minerals are oxidized to sulfate. Thus, sulfur does not leave the system.
- Alkaline components such as $CaCO_3$ or CaO do not retain organic sulfur even when present at the 6% w/w level.
- The presence of iron and large amounts of nitrate does not interfere with the $BaSO_4$ procedure for total inorganic sulfur. The standard procedure to remove these possible interferences results in reduced recoveries and an increase in the variance.
- The pH in the $BaSO_4$ precipitation must be adjusted to 1 to avoid excessive solubilization of $BaSO_4$. A pH greater than 1 can result in the precipitation of iron in certain cases.
- Sulfur forms analysis can be made on liquified coal which cannot be analyzed by the ASTM procedure.

A detailed examination of the precision and accuracy of the proposed method with the ASTM D2492, the proposed ASTM atomic absorption (AA) modification to D2492, the TRW AA method, the Leco combustion method for total sulfur, and the new plasma ashing method has shown that:

- Total inorganic sulfur can be determined with a precision of ±0.02% as compared to ±0.05-0.08% for the ASTM procedure.
- The precision for proposed ASTM AA modifications of the ASTM D2492 for pyritic iron is 0.06-0.07% as compared to 0.01-0.02% for the TRW-AA procedure. The TRW method uses a less sensitive iron line and includes a short curve method for instrument calibration.

- The Leco combustion method gives results equivalent to the Eschka method but with a reduction in precision from ±0.02-0.03% to ±0.06%.

- Discrepancies between the actual values obtained by the ASTM method and the plasma ashing method have been resolved in favor of the plasma ashing method.

- Agreement between the ASTM-AA method and especially the ASTM-TRW-AA method is generally better than with the ASTM D2492.

The feasibility of a direct organic sulfur analysis by plasma oxidation with subsequent trapping of the organic SO_x species on solid sorbents placed in the exit port of the plasma reaction chamber has also been demonstrated.

2. RECOMMENDATIONS

The following recommendations are made:

- The oxygen plasma coal sulfur forms analysis procedure should be further tested under "round robin" conditions to determine variability between laboratories.

- A larger cross section of coal regions and seams should be analyzed in replicate with results compared to ASTM D2492.

- Additional liquified coal samples, and samples obtained from other types of coal desulfurization systems should be analyzed by both the plasma and ASTM procedure (where applicable) and results compared.

- A separate program should be initiated to develop the direct determination of organic sulfur using the plasma technique and the concept of solid sorbents. The effort should be scoped to include hardware as well as methods development/optimization and also investigation of other organically bound species such as nitrogen and halogens.

3. INTRODUCTION

The need to reduce SO_x emissions from the burning of coal as mandated by the Clean Air Act has stimulated strong interest in the development of new or improved methods of physical and chemical coal cleaning. Many of these methods are specific to either the inorganic or organic form of sulfur in coal. As these processes are optimized or developed, it becomes increasingly more important to have an accurate and precise sulfur forms analysis to delineate the effects of process modifications on sulfur removal. The present ASTM procedure, D2492, for sulfur forms determines total sulfate and pyritic sulfur.[1] Organic sulfur is determined by subtraction of the inorganic sulfur forms from the total sulfur. As a result, the organic sulfur value reflects the errors of all three analyses.

A survey of the existing literature and recognized authorities in the fields of coal cleaning and analysis indicated a general dissatisfaction with the present procedures. The results of the literature survey are documented in detail in Appendix A. The responses from workers in this field ranged from "anything is better" to the need for ±1% relative precision and accuracy for kinetic studies. Based on this survey, it was determined that the following would be desirable in a procedure.

- Increase the accuracy and precision of the inorganic sulfur extraction by removing all inorganic sulfur forms by a single ash extraction. This reduces coal matrix effects and the number of manipulations.
- Increase the accuracy and precision of the inorganic sulfur determination by using a single $BaSO_4$ gravimetric procedure. This procedure is very well developed and capable of very high precision and accuracy.
- Retain the capability of inorganic sulfur forms analysis.
- Develop a method for direct analysis of organic sulfur.

Figure 1 shows the sulfur forms present in coal and Figure 2 shows the sequence used in the ASTM procedures. Total sulfur is determined by the Eschka method ASTM D271 and pyritic and sulfate sulfur is determined by ASTM method D2492. The Eschka procedure is highly accurate and precise

Sulfate ($FeSO_4$)	— Present in most coals as a result of oxidation (weathering of pyrite).
Pyrite (FeS_2)	— Present in minor to major amounts in all coals. Found both very finely dispersed and in occlusions.
Sulfide (FeS)	— Found only in those coals that have been treated in a reducing atmosphere and in certain Illinois coals.
Organic Sulfur	— Organsulfur compounds present in all coal.

Figure 1. Sulfur Forms in Coal

- Determine total sulfur
- Extract $FeSO_4$ with HCl and determine sulfur gravimetrically
- Extract FeS_2 with HNO_3 and determine iron by dichromate or permanganate titration
- Determine organic sulfur by difference

Figure 2. ASTM Method for Sulfur Forms Determination

and for these reasons there is a general satisfaction with this procedure. The actual sulfur forms procedure, however, suffers from several sources of error which affect accuracy and precision which are tacitly recognized in the ASTM "precision" requirements listed in Table 1. The cumulative effect of these requirements for duplicate organic sulfur analyses is that they can be considered acceptable if they are with 0.01-0.2% when performed in the same laboratory or within 0.3-0.6% when performed in different laboratories.[1] TRW's experience with the Meyers Process is consistent with these results. A pooled standard deviation of ±0.09% for the organic sulfur determination was calculated for the analysis of 69 sets of coals in triplicate.[2]

Of the sources of error in ASTM Method D2492 listed in Figure 3, matrix effects in the pyritic sulfur determination are a major problem, which contributes greatly to the limited reproducibility of the method, as given in Table 1. The nitric acid extraction often removes substantial amounts of organic material. If not destroyed. this material is oxidized by dichromate or permanganate titrant in the determination of pyritic iron yielding a high result. (Pyritic iron must be determined because the nitric acid often removes some organic sulfur.) The manipulations to do this result in reduced precision. Often color still remains which results in a fading and indistinct endpoint requiring a high degree of operator experience and judgment. This problem is tacitly recognized by greatly expanded precision limits in Column 3, Table 1, where results between operations are compared.

A fundamental and more serious problem is many coals contain finely dispersed (< 5μ) pyrite which is in the form of single crystals or in spherical crystal assemblies (framboids)[3]. These particles may be occluded in coal particles or enclosed in a kaolin lattice which can retard or prevent their dissolution in the standard ASTM acid digestion procedure. This type of pyrite may be as much as 80% of the total pyrite in some coals which can cause incomplete or marginal extraction efficiency. Thus, experimental variables such as additional HNO_3 extraction time and additional or a different type of grinding of the coal can significantly affect the results

Table 1. ASTM Precision Requirements for Sulfur Forms Analysis[a]

Sulfur Form	Repeatability[b]	Reproducibility[c]
Total		
Less than 2%	0.05	0.10
More than 2%	0.10	0.20
Sulfate[d]	0.02	0.04
Pyritic		
Less than 2%	0.05	0.30
More than 2%	0.10	0.40
Organic (difference)		
Worst Case	0.22	0.34
Best Case	0.12	0.64

(a)Total sulfur, ASTM D271; sulfate and pyritic sulfur, ASTM D2492.[1]

(b)Consecutive determinations on the same sample, in the same laboratory, with the same operator and apparatus.

(c)Separate determinations carried out on representative samples in different laboratories.

(d)Usually less than 0.2% in freshly mined coal.

HCl Extraction

- Incomplete non-pyritic iron extraction which is extracted in the next step

HNO_3 Extraction for Pyrite, FeS_2

- Incomplete extraction FeS_2 due to matrix effects
- Incomplete washing of coal to remove Fe^{+++}
- Organic matter extracted from coal can interfere with end point of titration
- Addition of excess $SnCl_2$ to reduce Fe^{+++} to Fe^{++} can interfere with final titration
- If all coloration is not destroyed, the final end point may fade or be difficult to observe

Figure 3. Error Sources in ASTM Method D2492

by changing the amount of pyrite extracted. Coal ground to 60 mesh x 0 (ASTM specification) has a maximum particle size of 250 μ and it is very difficult to grind samples sufficiently to ensure total pyrite exposure. The net result is that unextracted pyrite is counted as organic sulfur. The experience of TRW and the Illinois Geological Survey (IGS)* indicates that this is a common problem with Eastern Interior Basin coals although it also occurs with coals from other regions. The significance of this problem can be put in perspective when it is realized that all processes designed to remove organic sulfur also remove inorganic sulfur. Thus, if a significant portion of the "organic" sulfur is actually pyrite, the calculated organic sulfur removal in a given process will be significantly biased to the high side.

In order to alleviate these problems while maintaining the basic concepts of the ASTM methods, TRW has proposed a plasma ashing procedure which is the subject of this report. This method depends on the selective removal of the organic coal matrix including the organic sulfur via a low temperature oxygen plasma. This has the following advantages:

*Private communication with H. J. Kuhn, Illinois Geological Survey.

- Up to 90% of all matrix effects are eliminated.
- Very fine encapsulated pyrite is now available for extraction.
- A single HNO_3 extraction will remove all inorganic sulfur species that can be determined in a single analysis.
- The absence of organic sulfur in the ash allows the use of the much more accurate and precise $BaSO_4$ gravimetric procedure.
- ASTM D2492 can still be applied to the ash for separate sulfate and pyrite determinations.
- Measuring or trapping the SO_x species in the plasma asher exit gases allows for the possibility of the direct determination of organic sulfur.

The following sections describe the verification of this method for the direct determination of inorganic sulfur, inorganic sulfur forms, and the indirect determination of organic sulfur. Also included is a discussion of the successful proof-of-principle experiments for the direct determination of organic sulfur, and a text of procedures for sulfur forms measurement.

Appendix A contains a detailed report of the literature survey.

4. RESULTS

The results discussed in this section are divided into three parts. The first deals with the verification of the oxygen plasma procedure and the verification of the sulfur forms method, including organic sulfur by difference. The second part describes the application of the method described in Section 4.1 to liquified coal samples, and the third, Section 4.3, describes the proof-of-principle experimentation for the direct determination of organic sulfur.

4.1 COAL SULFUR FORMS ANALYSIS WITH INDIRECT DETERMINATION OF ORGANIC SULFUR

This analysis procedure is based on the selective removal of the organic matrix including organosulfur species from coal with a low temperature oxygen plasma. The inorganic sulfur species are quantitatively retained in the remaining ash. The inorganic sulfur in the ash is then extracted with dilute nitric acid and determined gravimetrically as $BaSO_4$ or speciated by ASTM D2492.

An evaluation of the data in the following sections shows that (1) the plasma procedure yields more accurate and precise results for inorganic and organic sulfur than the ASTM procedures; (2) naturally occurring sulfides are not affected under plasma conditions; and (3) organic sulfur species are not retained in the coal ash by reaction with alkaline compounds. The actual procedure has been optimized and is ready for testing in other laboratories.

4.1.1 Reactivity of Pyrite, FeS_2, and Other Naturally Occurring Sulfides

The major requirement of this method is the nonreactivity of pyrite and other possible naturally occurring sulfides to plasma oxidation. These can be oxidized to either the oxide or the sulfate. If oxidation to the oxide occurs, sulfur is lost resulting in high organic sulfur values and low inorganic sulfur values. Extensive oxidation to the oxide (>5%) could result in the failure of this procedure because of the inaccuracies that would be introduced. Oxidation to the sulfate causes the loss of one-half of the pyritic sulfur, but no loss to the other sulfide minerals. Although

this is not as serious, in most cases, the sulfur form is changed and the viability of the inorganic sulfur forms procedure would be compromised. Although both reactions are thermodynamically possible, preliminary evidence indicated that the reaction was kinetically controlled in that little or no conversion occurred. This conversion would be expected to proceed most rapidly at smaller particle sizes due to the larger surface area and possible heat buildup. Thus, it was considered essential to test FeS_2, FeS, PbS, and ZnS under actual plasma conditions using size fractions representing the lower size limit expected to be found in coal. Two different size fractions representing average particle sizes of approximately 3 and 9 microns were prepared by hand grinding under a nitrogen blanket. The actual average particle sizes shown in Table 2 were determined using a Fisher sub-siever sizer. Two hundred milligrams of each particle size were spread in a Petri dish and "ashed" for 3 days at 100 watts power, and 200 cc/min O_2, which is identical to the conditions used to decompose coal. At the end of 3 days, the samples were removed,

Table 2. Reactivity of Sulfide Minerals Under Ashing Conditions

Compound	Average Particle Size μ	Wt Change %	%S Converted to SO_4=	%S Converted to oxide(a)
PbS	3.5	+1.2	+0.06	N.D.
	9.0	+0.6	+0.08	N.D.
FeS	2.5	+4.5	+0.54	N.D.
	3.1	+2.0	+0.20	N.D.
ZnS	3.1	+1.0	+0.69	N.D.
	8.2	+1.0	+0.25	N.D.
FeS_2	2.3	--(c)	+0.1	N.D.(b)
	10.0	--(c)	No change	N.D.(b)

(a)N.D. = Not detected by X-ray diffraction, detection limit 1-2%.

(b)In carbon matrix to allow for even dispersion (see text).

(c)Carbon matrix does not allow computation of this value.

cooled in a desiccator, weighed (conversion to sulfate would result in weight gain and conversion to oxide in weight loss), the sulfate content determined turbidimetrically on a hot water extract of a weighed aliquot and the oxide formation investigated using an X-ray diffraction technique. Results are summarized in Table 2.

A small conversion to sulfate was obtained with FeS and ZnS with the percentage increase inversely proportional to the average particle size. In no case did the conversion to sulfate exceed 1% of total compound exposed. As conversion to sulfate does not result in any sulfur loss for these two compounds, there are no negative or positive analytical biases. In the case of FeS_2, however, the neat 2.3μ sample showed evidence of ignition to Fe_2O_3 in those areas where the dispersed sample formed small piles. In areas where the FeS_2 was smoothly dispersed no visible reaction occurred. Dispersal of the 0.2 g pyrite in 1 g of carbon (10% pyritic sulfur) completely eliminated this problem. This indicates that when extremely fine pyrite is present, the temperature of the ashing must be controlled such that autoignition cannot occur and that dispersal in a carbon matrix is sufficient to prevent this oxidation from occurring.

Conversion to oxides or other compounds was checked by X-ray diffraction. One hundred milligrams of plasma ashed minerals were dispersed ultrasonically in a collodian matrix and dispersed as a thin film on a glass slide. These samples were then analyzed by X-ray diffraction and the spectra compared to the ASTM powder diffraction file. Operating parameters were as follows:

GE XRD-5 Operating Parameters

Cu tube - 50 KVP, 20 ma
3° beam
Medium resolution soller slit
0.1° slit, Ni filter
Scan speed 2°/min
Proportional detector
Range setting linear, 500 cps

In no case was any change noted either as to shifts or appearance of additional lines that might be attributed to formation of oxides. An approximate detection limit of 1-2% for the respective oxides was established for each compound by adding a known weight of oxide and determining response.

4.1.2 Nonretention of Organic Sulfur by Alkaline Ash Constituents

Coal ash often contains considerable amounts of alkaline materials such as calcium carbonate, $CaCO_3$ and calcium oxide, CaO. These materials are used extensively in SO_x scrubbing media. Thus, it was considered essential to investigate the possibility of organic sulfur retention by these materials. In order to do this with the highest degree of precision and accuracy, demineralized coal containing only organic sulfur was used. These samples, #C-18572 and #C-18844 obtained from the Illinois State Geological Survey (IGS), had organic sulfur contents of 1.81% and 1.17%, respectively. They were doped with 3% and 6% w/w $CaCO_3$, or CaO, and ashed under standard conditions (3 days, 100 watts rf power, and 200 cc/min oxygen flow). After ashing, they were extracted with 1:1 HCl and sulfate was determined turbidimetrically. The results in Table 3 show that in no case did the sulfate content increase as a result of the ashing procedure. Thus, SO_x retention can be eliminated as an interference in this procedure.

Table 3. Possible Retention of Organic Sulfur in Plasma Ash

Coal	Initial Sulfate Analysis	Plasma Ashed Sulfate Analysis			
		$CaCO_3$, % w/w		CaO, % w/w	
		3%	6%	3%	6%
C-18844B	0.05	0.03	0.05	0.03	0.07
C-18572B	0.10	0.08	0.07	0.08	0.05

4.1.3 Optimization of Plasma Ashing Procedure - Parameter Verification Studies

The size of the container used in the plasma ashing step and the gravimetric procedure used for sulfate determination for the initial studies described in Section 4.1.5 were chosen because they had given satisfactory results in past studies. Although this procedure appeared satisfactory, it was essential that further parametric verifications be conducted so that sensitive areas, if any, in the procedure could be identified and corrected. This section evaluates (1) the effect of pH on the precipitation of $BaSO_4$, (2) the effect of container size, and (3) the possible use of the entire Eschka procedure on the plasma ash for increased precision and accuracy.

Because $BaSO_4$ has a slight solubility in acid solutions, it is necessary to neutralize most of the HNO_3 present in the acid extract of the ash. Sufficient acid must be present, however, to prevent the coprecipitation of iron. Prior experience indicated that a pH of approximately 1 is sufficient to allow quantitative precipitation of $BaSO_4$ and prevent interferences from iron. It was the purpose of this experimentation to more closely define the pH adjustment step. This experimentation was performed in parallel with experimentation on the effect of the size of ashing containers on sample recovery. Purging and evacuation of the plasma reaction chamber can disturb ash if care is not taken. A larger ashing container could alleviate this problem. In addition, a separate series of samples was analyzed using the Eschka technique. With the latter technique, the resulting ash was transferred quantitatively from the containers, mixed with Eschka mixture, and analyzed by ASTM D271.

Quadruplicate samples were used for each condition studies. The 65 x 35 mm. ashing containers were fabricated from 250 ml Pyrex beakers. These containers were also used for the $BaSO_4$ precipitation pH studies. The results of these studies, summarized in Table 4, show that at pH 2 significant amounts of iron oxides can be precipitated and invalidate the results. Thus, it is important to carefully adjust the pH to 1 in order to prevent excessive solubilization of $BaSO_4$ at a lower pH and interferences caused by coprecipitation of iron at a higher pH. Comparison

Table 4. Total Inorganic Sulfur Analysis-Parametric Procedure Verification Studies

Coal Sample		Total Inorganic Sulfur, % w/w[a]		
		60x15 mm Container pH 1	65x35 mm Container pH 1	65x35 mm Container pH 2
Martinka Mine Lower Kittanning Seam		2.59	2.58	Iron precipitate formed analysis discontinued
		2.59	2.59	
		2.57	2.55	
		2.54	2.54	
	Average	2.57	2.56	
	Standard Deviation	±0.024	±0.024	
	% RSD[b]	0.93	0.94	
Delmont Mine, Upper Freport Seam				Eschka Procedure[c]
		4.14	4.05	3.96
		4.02	4.23	4.14
		4.07	4.09	4.10
		4.06	4.08	3.98
	Average	4.07	4.11	4.04
	Standard Deviation	±0.050	±0.080	±0.090
	% RSD	1.23	1.95	2.22

(a) All samples extracted with 1:7 HNO_3 except where noted.

(b) RSD = Relative Standard Deviation

(c) Ash analyzed by standard Eschka procedure, ASTM D271.

of results between the two sizes of containers showed no significant difference in total inorganic sulfur found. Ashing time was found to increase with use of high form containers, hence the use of standard petri dishes is recommended. The Eschka combustion procedure (ASTM D271) was used on a separate set of plasma ashed Delmont coal samples. These results were compared to the pH 1 data for the same coal in Table 4 and found to be significantly less precise. In addition, the % relative standard deviation for the Eschka procedure is substantially poorer than with any other data set in Table 4. The reason for this poor precision may be due to inherent difficulties in transferring fine, dry ash into the Eschka mixture by brushing.

4.1.4 Optimization of Plasma Ashing Procedure - Interferences Due to Iron and Nitrate

The procedure used in Section 4.1.5 involves the precipitation of $BaSO_4$ in the presence of significant amounts of Fe^{+++} and NO_3^- ions. These ions can be troublesome because of the possibility of coprecipitation of $Fe_2(SO_4)_3$ and $Fe(NO_3)_3$.[4] On ignition $Fe_2(SO_4)_3$ is converted to Fe_2O_3, Equation (2). This results in one equivalent weight of $SO_4^=$ being converted into a gravimetric product with an equivalent weight of 53.2 instead of the equivalent weignt of $BaSO_4$ of 233.4. This loss of weight results in low values. The coprecipitation of $Fe(NO_3)_3$ and conversion to Fe_2O_3, Equation (3), represents a weight gain and yields high values.

$$\begin{array}{lll} & BaSO_4 \xrightarrow[\text{ignition}]{925^\circ C} & BaSO_4 \\ \text{E.W.} & 233.4 & 233.4 \end{array} \qquad (1)$$

$$\begin{array}{lll} & 1/3\ Fe_2(SO_4)_3 \xrightarrow[\text{ignition}]{925^\circ C} & 1/3\ Fe_2O_3 + 3SO_2 \\ \text{E.W.} & 133.2 & 53.2 \end{array} \qquad (2)$$

$$\begin{array}{lll} & Fe_2(NO_3)_3 \xrightarrow[\text{ignition}]{925^\circ C} & Fe_2O_3 + 3NO_2 \\ \text{E.W.} & 201.7 & 159.7 \end{array} \qquad (3)$$

The simple removal of iron by precipitation with NH_4OH and filtration is not possible because the presence of HNO_3 promotes the formation of a very fine precipitate which is very difficult to filter. ASTM E350 is a procedure which uses a HNO_3 dissolution followed by a $BaSO_4$ precipitation to analyze for sulfur in ferrous metals.[5] In this procedure, these interferences are removed first by evaporation of the solution to dryness after neutralization with $NaCO_3$, and then redissolving the salts. Fe^{+++} is reduced to Fe^{++} with zinc. The pH is adjusted to ~4, with methyl orange as indicator, followed by the addition of $BaCl_2$.

This method was compared to the one which was in use by adding aliquots of standardized $Fe_2(SO_4)_3$ (dichromate titration of iron) solution to 25 ml of 1:7 HNO_3 and analyzing the resulting solutions by both methods. Solution concentrations were chosen to simulate inorganic sulfur concentrations in whole coal of ~0.4 and 2.6%. In a separate experiment, the effect of an additional 0.7% nonpyritic iron was evaluated by doping the ferric sulfate solutions with ferric chloride. Results, which are the averages of 10 determinations, are summarized in Table 5. These data indicate that while both methods appear to be equally precise, recovery for the simple precipitation at pH 1 method averaged 98 ±3% while the more complex ASTM E-350 method gave average recoveries of 90 ±4%. For the simplified method, only in the low sulfur case with added iron was the recovery less than 90%, while the complex method yielded recoveries of 83-84%. It is also estimated that the complex method requires three times the labor of the simplified method. Thus, the simplified procedure is being recommended for use.

4.1.5 Preliminary Evaluation of Plasma Ashing Procedure

Preliminary evaluation of the procedure was performed on 13 coals. The coals chosen represent "problem coals" because of sulfur mass balance problems found during Meyers' processing (TRW technique for removal of pyritic sulfur by treatment with ferric sulfate).[2] As such, they represent a worst case test of the method. Organic sulfur values listed in Table 1 were calculated by difference using three methods for inorganic sulfur determination. For the whole coal extraction, ASTM D2492 was used to determine both sulfate and pyritic iron. In addition to the titrimetric

Table 5. Comparison of Gravimetric Sulfate Procedures

Test Conditions	mM Sulfur* in Aliquot	Simplified Method pH/Adjustment		Complex Method (ASTM -350)	
		mM Sulfur	% Recovery	mM Sulfur	% Recovery
Near $Fe_2(SO_4)_3$	0.1202	0.118	97	0.100	83
	±0.0006	±0.0038	±3.2	±0.0078	±6.5
	0.801	0.805	100	0.742	93
	±0.0040	±0.0088	±1.1	±0.0097	±1.2
$Fe_2(SO_4)_3$ plus 0.13 mM $FeCl_3$	0.1230	0.112	91	0.110	89
	±0.0006	±0.0067	±5.4	±0.0036	±2.9
	0.820	0.813	99	0.770	94
	±0.0040	±0.012	±1.5	±0.0097	±1.2
Average		S=0.0084	98 ±3	S=0.008	90 ±4

*As calculated from the iron content which was determined by dichromate titration

determination of iron an atomic absorption method, developed at TRW and described in Section 5, was also tested. Total inorganic sulfur in the plasma ashed sample was determined by the $BaSO_4$ gravimetric procedure in Section 5. All organic values were calculated by subtraction of the appropriate values from a common total sulfur value.

The organic analysis results, Table 6, show that when the results are evaluated by coal basins, the ASTM-TRW-AA* and plasma ashing procedures give essentially identical results while the standard ASTM procedure is low by 5-6%. In the case of the interior basin coals, the ASTM procedures are in good agreement while the plasma procedure is low by 10%. According to Dr. Anthony of the Old Ben Coal Company, three of these coals are from the same area and it has been demonstrated that they contain pyritic sulfur that is unextractable by the ASTM procedures. If this unextractable inorganic sulfur were extracted from the plasma ashed sample, this would be the cause of the low organic number. Most of the Appalachian coals in this table are also "problem" coals from Meyers' processing. When before and after treatment values are compared, both the plasma ashing and the ASTM-TRW-AA procedures give consistent results, while the ASTM procedure gives widely discrepant results that tend to be significantly low for untreated Appalachian coals. Thus, in reference to evaluation of coal cleaning processes, it appears that the ASTM procedure gives results dependent on coal processing while the other two procedures give results that are virtually independent of the history of the coal.

4.1.6 Comparative Evaluation of Proposed Procedure with ASTM Methods

The comparative evaluation of the proposed procedure with ASTM methods was performed on coals in triplicate. These were chosen to represent a variety of ten seams in the Appalachian and Eastern Interior coal basins. Each coal was analyzed by the Eschka method, ASTM D271, for total sulfur, ASTM D2492 for sulfur forms, and the plasma ashing procedure in Appendix B. Analysis of the HNO_3 solution obtained from extraction of the

*This designation is used to distinguish this method from a similar method proposed by ASTM.

Table 6. Comparison of Organic Sulfur Determinations
(% w/w by Difference)

Mine/Seam	Treated(T)[a] Untreated(U)	ASTM Procedure		Plasma Ashed
		Std.	TRW-AA	
E Seam (ROM)	U	0.48	0.46	0.52
	T	0.57	0.66	0.59
E Seam (Cleaned)	U	0.51	0.57	0.60
	T	0.60	0.68	0.65
Delmont (Upper Freeport)	U	0.25	0.79	0.81
	T	0.74	0.74	0.64
Bird (Lower Kittanning)	U	0.22	0.54	0.62
	T	0.50	0.55	0.55
Egypt Valley (Pittsburgh)	U	1.34	1.78	1.97
	T	2.03	1.81	1.81
Fox (Lower Kittanning)	T	1.18	0.90	0.90
	T	1.18	0.91	0.92
Williams (Pittsburgh)	U	1.19	1.48	1.42
	T	1.38	1.40	1.41
Lucas (Middle Kittanning)	U	0.32	0.50	0.49
Brookdale #77 (Lower Kittanning)	U	0.48	0.48	0.46
Old Ben #21[b] (Illinois #6)	U	0.63	0.60	0.45
Old Ben #24[b] (Illinois #6)	U	1.66	1.57	1.57
Old Ben #26[b] (Illinois #6)	U	1.38	1.34	1.19
Inland Steel[b] (Illinois #6)	U	1.81	1.80	1.66

(a) Treated by Meyers Process to remove pyritic sulfur and adjusted for mineral matter (ash) changes.

(b) Eastern interior basin coals.

coal was analyzed by the standard titrimetric procedure and a new atomic absorption procedure which is being circulated for comment by ASTM. This should be distinguished from the TRW atomic absorption procedure which uses a different iron absorption line (Section 4.1.7). The results are tabulated in Table 7. The total inorganic sulfur values are summarized in Tables 8 and 9; the organic sulfur values were calculated by difference.

From Table 7 it is seen that the ASTM titrimetric pyritic sulfur values exhibit a distinct negative bias when compared to values determined by AA. The exact reason for this bias is difficult to explain because the pyritic iron was determined on aliquots of the same extract for both procedures. In addition, the same iron standard was used for calibration of both analytical procedures. One explanation is loss of iron during the iron hydroxide precipitation, filtration and redissolution step which is necessary for the titrimetric procedure but not for the AA determination. This explanation is consistent when the total inorganic values (sulfate sulfur and pyritic sulfur) determined using the two ASTM procedures are compared to the TRW plasma-total inorganic values (Table 8); the results using the AA technique are in excellent agreement with the values obtained in the plasma ash procedure for the Appalachian coals. This agreement for total inorganic sulfur is directly reflected in the organic sulfur values contained in Table 9. The ASTM analyses of Eastern Interior Coals as represented by Old Ben No. 21, 16 and Inland Peabody exhibit a positive bias for organic sulfur when compared with the plasma procedure. This bias probably is the result of the presence of very fine ($< 5\mu$) occluded pyrite present in these coals which is not extracted with nitric acid in the ASTM procedure. This is substantiated by the electron probe microanalysis studies described in Section 4.1.8 and by private communications with A. V. Marse of Old Ben Coal Company and H. J. Kuhn of the Illinois Geological Survey. The presence of very fine occluded pyrite can also explain the large differences in total inorganic sulfur experienced with the tailings sample.

Table 7. Comparison of Sulfur Forms Analysis Methods

Mine	Coal Seam	Coal Basin	Total Sulfur		Pyritic Sulfur[a]-ASTM		Sulfate Sulfur[c] ASTM	Total Inorganic TRW Plasma Ash
			Eschka	Leco	Titration[c]	AA[b]		
Old Ben #21	Illinois #6	Eastern Interior	1.11 ±0.032	1.28 ±0.030	0.32 ±0.045	0.48 ±0.066	0.08 ±0.000	0.71 ±0.011
Old Ben #26	Illinois #6	Eastern Interior	2.26 ±0.031	2.21 ±0.031	0.65 ±0.036	0.77 ±0.006	0.16 ±0.006	1.25 ±0.015
Inland Peabody	Illinois #5	Eastern Interior	3.24 ±0.012	3.11 ±0.071	0.94 ±0.028	1.03 ±0.006	0.38 ±0.012	1.59 ±0.015
Martinka	L. Kittanning	Appalachian	1.59 ±0.058	1.59 ±0.059	1.16 ±0.097	1.33 ±0.130	0.12 ±0.006	1.49 ±0.015
E-Seam	U. Freeport	Appalachian	1.04 ±0.015	1.06 ±0.025	0.25 ±0.010	0.34 ±0.006	0.08 ±0.006	0.40 ±0.036
C-Prime	U. Kittanning	Appalachian	1.52 ±0.032	1.42 ±0.040	0.74 ±0.040	0.90 ±0.007	0.08 ±0.000	0.96 ±0.006
Mathies	Pittsburg	Appalachian	1.60 ±0.020	1.52 ±0.075	0.57 ±0.026	0.66 ±0.006	0.47 ±0.021	1.20 ±0.010
Lucas	M. Kittanning	Appalachian	1.70 ±0.025	1.69 ±0.044	0.67 ±0.006	0.82 ±0.006	0.44 ±0.006	1.19 ±0.011
Muskingum	Meiggs Creek #9	Appalachian	5.71 ±0.051	5.62 ±0.061	1.87 ±0.066	2.42 ±0.040	1.22 ±0.092	3.33 ±0.040
Tailings from Central Ohio Coal Co.	Meiggs Creek #9	Appalachian	3.28 ±0.035	3.31 ±0.096	1.87 ±0.074	1.92 ±0.170	0.02 ±0.000	2.52 ±0.035
		Pooled Std. Dev.	0.034	0.058	0.051	0.072	0.030	0.023

[a] Extraction performed by ASTM D2492; both analysis were performed on same solution.

[b] The proposed ASTM Atomic Absorption procedure was used.

[c] ASTM D2492.

Table 8. Total Inorganic Sulfur Comparison[a]

Coal	ASTM Titration[b]	ASTM AA[c]	TRW Plasma
Old Ben #21	0.40	0.56	0.71
Old Ben #26	0.81	0.93	1.25
Inland Peabody	1.32	1.41	1.59
Martinka	1.28	1.45	1.49
E-Seam	0.33	0.42	0.40
C-Prime	0.82	0.98	0.96
Mathies	1.04	1.13	1.20
Lucas	1.11	1.26	1.19
Muskingum	3.09	3.64	3.33
Tailings from Central Ohio Coal Co.	1.89	1.94	2.52
Pooled Standard Deviation	±0.059	±0.078	±0.023

(a) Sum of sulfate and pyritic sulfur for the ASTM methods and determined directly in the plasma ashing method.

(b) ASTM sulfate sulfur plus pyritic sulfur determined by titration of pyritic iron.

(c) ASTM sulfate sulfur plus pyritic sulfur determined by the proposed ASTM procedure for determination of iron by atomic absorption.

Table 9. Organic Sulfur

Coal	ASTM		TRW
	Titration	AA	Plasma
Old Ben #21	0.71	0.55	0.40
Old Ben #26	1.45	1.33	1.01
Inland Peabody	1.92	1.83	1.65
Martinka	0.31	0.14	0.10
E-Seam	0.71	0.62	0.64
C-Prime	0.70	0.54	0.56
Mathies	0.56	0.47	0.40
Lucas	0.59	0.44	0.51
Muskingum	2.62	2.07	2.38
Tailings from Central Ohio Coal Co.	1.39	1.34	0.76
Pooled Standard Deviation	±0.058	±0.085	±0.041

The standard deviation for each set of triplicate analyses was calculated and then used to calculate the standard deviation for total inorganic sulfur and organic sulfur as follows:

$$\sigma_{Inorganic} = \sqrt{\sigma^2_{SO_4} + \sigma^2_{FeS_2}} \qquad (1)$$

for ASTM D2492 and sulfur form on plasma ash,

$$\sigma_{Organic} = \sqrt{\sigma^2_{total} + \sigma^2_{SO_4} + \sigma^2_{FeS_2}} \qquad (2)$$

for ASTM D2492, and

$$\sigma_{Organic} = \sqrt{\sigma^2_{Total} + \sigma^2_{Inorganic}} \qquad (3)$$

for the plasma ashed sample with no inorganic sulfur speciation.

In addition, the pooled standard deviation for each set of 10 triplicate samples was calculated. When a sufficient number of data sets are used, this value gives an estimate of the precision that can be expected from an analysis method on a long term basis. The formula for this calculation is given in Equations (4) and (5). For organic sulfur, the value calculated from either Equation (2) or (3) was used.

$$\sigma = \sqrt{\frac{\phi_1 \sigma_1^2 + \phi_2 \sigma_2^2 + \phi_3 \sigma_3^2 + \text{----}}{\phi_1 + \phi_2 + \phi_3 + \text{----------}}} \qquad (4)$$

where

σ = standard deviation

ϕ = number of values used to calculate σ.

Thus, when ϕ is the same for all σ, Equation (4) reduces to

$$\sigma = \sqrt{\frac{\sum_{1}^{n} \sigma_n^2}{n}} \qquad (5)$$

where

n = number of data sets.

As can be seen in Table 7, the pooled standard deviations for the plasma total inorganic sulfur, Eschka total sulfur, and sulfate sulfur analysis are similar. This is to be expected because all three are similar gravimetric analyses. The lower value for the plasma inorganic most

likely reflects the fewer manipulations and/or lack of coal matrix effects in these samples. Table 8 summarizes the total inorganic sulfur results calculated by all three methods. For the ASTM procedures, this is the sum of the pyritic and sulfate sulfur. It is apparent from the tabulation that the plasma ashing procedure offers a substantial increase in precision over the other two methods.

Table 9 tabulates the organic sulfur corresponding to pooled standard deviation values calculated by all three methods. Although these values are all "diluted" by a common total sulfur value, the plasma ash number is still better than both ASTM values. The ASTM titration value is within 50% of the plasma ash value, but it must be remembered that there are accuracy problems associated with this method. If the pooled standard deviation for the Eschka technique is set identical to the plasma ash inorganic value, the corresponding values are ±0.033 and ±0.081 for the plasma ash and ASTM-AA techniques, respectively. It is felt that this assumption is valid if extra care is taken with the Eschka technique. Thus, it can be seen that the plasma ash method offers a substantial increase in both the precision and accuracy of coal sulfur forms analysis.

4.1.7 Comparative Evaluation of Inorganic Speciation

Addition experimentation was performed on the 10 coals discussed in Section 4.1.6 to test the application of the ASTM sulfur forms extraction procedure on the plasma ash and to compare the corresponding analysis of the whole coal. ASTM D2492 was used for both sulfate extraction and analysis. The analysis of pyritic iron in the HNO_3 extract was performed by atomic absorption in both cases. However, because of the poor precision of the proposed ASTM-AA method (Section 4.1.6), the TRW-AA method which has given excellent precision in other work was used.[2] The principal deviations in this method are the use of the less sensitive iron line at 244.0 nm, the use of a bracketing technique for instrument standardization, and the omission of lanthanum as a background suppressant. These analyses, performed in triplicate, are presented in Table 10. The whole coal and direct total inorganic results have been taken from Table 8. The last three columns of this table compare total inorganic sulfur calculated using three procedures: (1) ASTM procedure, (2) plasma ash procedure with

Table 10. Comparison of Inorganic Speciation Methods

Coal	Sulfate Sulfur		Pyritic Sulfur (AA)		Total Inorganic Sulfur		
	ASTM	Plasma	ASTM (AA)	Plasma	ASTM[a]	Plasma[b]	Plasma[a]
Old Ben 21	0.08 ±0.000	0.22 ±0.015	0.48 ±0.066	0.41 ±0.013	0.56	0.71 ±0.011	0.63
Old Ben 26	0.16 ±0.006	0.29 ±0.064	0.77 ±0.000	0.91 ±0.010	0.93	1.25 ±0.015	1.20
Inland Peabody	0.38 ±0.012	0.53 ±0.074	1.03 ±0.006	1.17 ±0.024	1.41	1.59 ±0.015	1.70
Martinka	0.12 ±0.006	0.23 ±0.002	1.33 ±0.130	1.12 ±0.002	1.45	1.49 ±0.015	1.35
E-Seam	0.08 ±0.006	0.10 ±0.006	0.38 ±0.006	0.27 ±0.004	0.42	0.40 ±0.036	0.37
C-Prime	0.08 ±0.000	0.16 ±0.009	0.90 ±0.007	0.87 ±0.017	0.98	0.96 ±0.006	1.03
Mathies	0.47 ±0.021	0.59 ±0.028	0.66 ±0.006	0.57 ±0.011	1.13	1.20 ±0.010	1.16
Lucas	0.44 ±0.006	0.47 ±0.013	0.82 ±0.006	0.96 ±0.040	1.26	1.19 ±0.011	1.43
Muskingum	1.22 ±0.092	1.25 ±0.040	2.42 ±0.040	2.20 ±0.041	3.64	3.33 ±0.040	3.45
Tailings	0.02 ±0.010	0.44 ±0.020	1.92 ±0.170	2.04 ±0.000	1.94	2.52 ±0.035	2.48
Pooled Std. Dev.	±0.030	±0.036	±0.068	±0.021	±0.078	±0.023	±0.042

(a) Sum of sulfate and pyritic sulfur

(b) HNO_3 extraction and gravimetric sulfate

direct gravimetric sulfate analysis, and (3) plasma and ash procedure using the sum of the sulfate sulfur and pyritic sulfur determined sequentially. Referring to Table 10, the following observations can be made:

- Sulfate sulfur values are comparable between methods for the Appalachian coals. (The single exception is the tailings sample.) The Eastern interior coals all exhibit a higher sulfate content using the plasma procedure. These results indicate that both pyritic and sulfate sulfur can occur in very fine occlusions that are difficult to extract by the ASTM procedure as applied to whole coal.

- Plasma ash pyritic sulfur was determined using a TRW atomic absorption iron procedure which is substantially different than the ASTM procedure. The pooled standard deviation of the TRW procedure was calculated at ±0.021 as compared to ±0.068 for the ASTM procedure. This shows a substantial improvement in precision over the ASTM procedure.

- Comparison of pyritic sulfur values is seen to follow the postulated trend with the Eastern interior coals (with the exception of Old Ben #21) exhibiting a higher plasma pyritic content than the ASTM values. Four of the Appalachian coals show excellent agreement in pyritic sulfur comprarison. The Martinka, Lucas and Muskingum coals show some deviation from expected values. The reason for this poor comparison is unknown.

- The last three columns of Table 10 compare the total inorganic sulfur values from each of the three techniques used. Comparison of these values shows the expected trend, i.e., high total inorganic values for Eastern Interior coals using the plasma procedures and agreement in values for Applachian coals (except the tailings sample). A least squares linear regression analysis was performed to compare the total inorganic values obtained using the two plasma procedures. This results in a correlation coefficient of 0.992, a slope of 1.03 and an intercept of -0.028 showing the excellent agreement between the two methods.

- The double analysis required for inorganic speciation results in a change in precision from ±0.023 to ±0.042. Thus, the most precise value for organic sulfur is obtained when a single total inorganic sulfur analysis is used.

4.1.8 Electron Probe Microanalysis of Coal Extracted by ASTM Procedure

The hypothesis that the divergence between procedures is the result of very fine pyrite, which is unextractable by the ASTM technique, was investigated by electron probe microanalysis. Samples of Old Ben #21,

Old Ben #26, and the tailings sample which was extracted by the ASTM technique were dried and prepared for analysis. These were selected because they exhibited the largest deviation in total inorganic sulfur values (Table 10). E-Seam coal was also analyzed as a baseline coal because no difference in total inorganic sulfur was observed for this coal.

Ten individual areas (approximately 30 A in diameter) across the diameter of the specimen were analyzed simultaneously for Fe and S. Individual values for each sample were averaged and concentrations calculated using pyrite as a standard. These are summarized in Table 11. As the electron probe analysis is an X-ray fluorescence technique these values should be considered as semiquantitative only. The organic sulfur values were calculated by assuming all iron is present as pyrite and subtracting an equivalent number of m moles of sulfur from the total sulfur. These values can be compared to those in Table 9 where the organic sulfur values obtained by the three different methods are summarized. Old Ben #26 and the tailings sample, both of which exhibited the largest difference in sulfur, do in fact contain measurable amounts of Fe. If this iron is considered to be unextractable pyrite, then the difference in organic sulfur values is easily explained. Neither the E-Seam or Old Ben #21 coals showed the presence of iron. This was expected for the E-Seam coal as the ASTM and plasma total inorganic values were in excellent agreement. The Old Ben #21 should have shown the presence of approximately 0.1% iron. This concentration level is at the approximate detection limit and explains why none was found.

Table 11. Electron Probe Microanalysis of HCl/HNO_3 Extracted Coals

Coal	S Analysis	Fe Analysis	Calculated Organic S
Old Ben #21	0.5	0.06	0.5
Old Ben #26	1.5	0.2	1.3
E-Seam	0.7	0.06	0.7
Tailings Sample	1.4	0.8	0.5

The microprobe analysis clearly illustrates the presence of residual iron in extracted coals, showing deviations in organic sulfur values between methods. This is a strong indication of the inability of the ASTM procedure to completely remove what is probably very fine occluded pyrite. The plasma procedure liberates this pyrite from the coal matrix, thereby facilitating its dissolution via nitric acid attack.

4.2 SULFUR SPECIATION IN LIQUIFIED COAL SAMPLES

The present state of the art for coal analysis is seriously deficient for the sulfur forms analysis of samples in which the coal matrix has been altered significantly. This includes coke, gasified or partially gasified coal, and liquified coal samples. The problem lies in the fact that the ASTM procedure relies on the assumption that the inorganic sulfur species can be extracted from the surface or by penetration of the acid into the coal pores. Thus, anything that changes the coal structure significantly alters the basis for this assumption. Liquified coal is the worst case because coal is changed into a liquid and as a result the inorganic species are coated with a hydrophobic liquid. The plasma ashing procedure avoids this problem by removing the organic matrix before any analysis is attempted. In the experiments listed below no inorganic speciation was attempted because the inorganic sulfur was expected to be very low and the conditions under which the product was produced were expected to convert all inorganic sulfur into iron sulfide, FeS.

Four liquified coal samples obtained from Sandia Corp. of Albuquerque, New Mexico, were analyzed for total, inorganic, and organic (by difference) sulfur content using the oxygen plasma analytical procedure. The coal samples were prepared by Sandia using 100 mesh x 0 coal in a creosote oil solvent at a solvent:coal(daf) ratio of 2.3:1. The initial (cold) hydrogen pressure in each case was 1000 psig, and the time at temperature was 30 minutes. Two samples were prepared from Illinois No. 6 coal (Orient No. 4 Mine) and two were from Kentucky No. 11 coal (Fies Mine). The filtered products were from runs that were carried out at 430°C, whereas the unfiltered ones were from 410°C runs. The samples are denoted as follows:

G98-57 FLP: Illinois No. 6, filtered product

G98-124 WLP: Illinois No. 6, unfiltered

G98-76 FLP: Kentucky No. 11, filtered

G98-106 WLP: Kentucky No. 11, unfiltered

Total sulfur analysis was obtained using the standard ASTM D271 Parr Oxygen Bomb procedure. Total inorganic sulfur was determined using the analytical procedure presented in Section 5 with slight modification to the oxygen plasma ashing step in order to prevent the volatile constituents in the liquified coal from frothing. This was done by first removing the volatile constituents under vacuum at 20 torr. When the initial frothing subsided, the vacuum was lowered to 0.5 torr and held for approximately 2 hours before ashing was initiated. The actual decomposition was performed at 50 watts input power and an oxygen flow of 400 cc/min; these conditions were chosen to minimize possible frothing losses through localized heating of the samples. The HNO_3 digestion and $BaSO_4$ precipitation were not changed. In addition to the sulfur speciation, the ash content was calculated. The results summarized in Table 12 show that in addition to removal of inorganic sulfur by filtration, substantial additional sulfur was removed in the 430°C filtered runs. The Illinois No. 6 results show that this method is capable of a high degree of precision, while the poor precision on the Kentucky No. 11 results probably indicates a degree of nonhomogeneity in the sample as the result of settling. It should be noted that this analysis indicates that both forms of sulfur varied under the experimental conditions employed. The form of sulfur that changes the most can be very important from an engineering point of view in order to avoid an expensive design modification that may not be appropriate. This type of information is not presently available from ASTM or other procedures.

4.3 DIRECT ORGANIC SULFUR DETERMINATION BY PLASMA ASHING AND SO_x SORPTION

One of the objectives of this task was to investigate the feasibility of determining organic sulfur directly. Development of such a system would be advantageous in that (1) a direct sulfur mass balance would be possible, (2) the necessity of performing an Eschka total sulfur and inorganic sulfur analysis would be eliminated, (3) direct determination

Table 12. Sulfur Forms Analysis of Liquified Coal

Sample Description	Sulfur Analysis, % w/w			Ash Content
	Total[(a)]	Total Inorganic[(b)]	Organic (by difference)	
Illinois No. 6				
Filtered	0.52 ±0.010	0.02 ±0.007	0.50 ±0.012	2.9, 2.6
Unfiltered	0.75 ±0.023	0.10 ±0.014	0.65 ±0.027	6.2, 9.0
Kentucky No. 11				
Filtered	0.67 ±0.112	0.02 ±0.014	0.65 ±0.187	3.6, 5.7
Unfiltered	1.11 ±0.136	0.06 ±0.021	1.05 ±0.138	5.4, 7.6

(a) Average triplicate determinations
(b) Average of duplicate determinations

would eliminate all the cumulative extraction and analysis errors, increasing the precision and accuracy of the analysis, and (4) if all four sulfur analyses (total, sulfate, pyritic, and organic) were performed directly, an error analysis of the individual analysis would be possible.

4.3.1 Introduction

The experimentation in this section is based on the fact that organo sulfur compounds contained in the coal matrix are converted into SO_x during the oxygen plasma decomposition. As discussed below, the preferred way of measurement is the use of solid sorbent because of the time for decomposition, vacuum conditions, and presence of oxygen and ozone in the exit gases. Preliminary experiments indicate excellent recoveries when molecular sieve or permanganate is used.

A literature search was undertaken to obtain information on solid absorbents or solid absorbent systems that had been used successfully for the sorption of SO_x species. These fall into two general categories: physical and chemical.[6] Physical sorption is further divided into adsorption and absorption. The former is primarily a surface phenomenon while the latter is characterized by diffusion into the pore structure of the sorbent. In chemisorption, the sorbed species react with the substrate to form actual chemical bonds and/or new and stable chemical species. Because of the generally weak bonds that occur in physical sorption systems, it was expected that chemisorption would be necessary for the vacuum system required for plasma ashing. Because this type of system generally has a low capacity compared to equivalent physical adsorption systems, the sorbent has to be specific. This is to avoid depletion of the sorbent by CO, CO_2, H_2O and NO_x which are present in large amounts in the exit gas stream.

The major portion of the literature deals with the sorption of SO_2 on substrates such as MgO,[7,8] silica gel,[9] cobalt oxide,[10] molecular sieves,[11] and MnO_2[12] at atmospheric or elevated pressure. None dealt specifically with SO_3 which is a product of the reaction of SO_2 with

molecular oxygen.[13,14] A single article discussed the determination of coal sulfur using ascarite and sodium hydroxide as solid sorbents.[15] However, the major portion of the work utilized a liquid nitrogen trapping system. Based on these data, Na_2CO_3, $NaHCO_3$, NH_4NO_3, KOH, CaO, and $KMnO_4$ deposited on silica gel and molecular sieve 13X were chosen for further evaluation.

4.3.2 SO_x Sorption – Experimental Procedure

Initial laboratory evaluations of several candidate sorbent systems were carried out using a nitrogen stream doped with SO_2. Sorbents were prepared by evaporating water solutions of the various species onto 40/80 mesh silica gel. The prepared sorbents were dried thoroughly and about 10g of each were packed into sorption tubes and held in place with quartz wool plugs at each end. Molecular sieve 13X was packed directly.

A small single chamber research plasma instrument was received on loan from International Plasma Corporation (IPC). A picture of the instrument is presented in Figure 4. This unit was used exclusively for testing solid sorbents under actual plasma conditions. Testing involved the introduction of a known volume of SO_2 into the oxygen plasma (instrument settings were those used for coal ashing) followed by trapping of generated species by solid sorbents contained in small canisters placed in the vacuum line as close to the exit port of the reaction chamber as possible. Figure 5 shows the assembled unit with the arrow indicating placement of the solid sorbent canister. Figures 6 and 7 show the configuration of the canisters in the outlet vacuum line.

The starting concentration of SO_2 in all experiments was obtained by recording the pressure (torr SO_2) bled into a known (150 cc) volume stainless steel pressure vessel. The concentration in mM ($\sim$0.5 for all runs) was calculated using the PV = nRT relationship. The SO_2 in the pressure vessel was then diluted to atmospheric pressure with N_2 and attached to an inlet line. The diluted SO_2 was then bled into the sorbents for the initial tests and into the plasma reaction chamber for the latter tests. The flow rate of the diluted SO_2 mixture was regulated to maintain an approximate one hour testing period. At the conclusion of

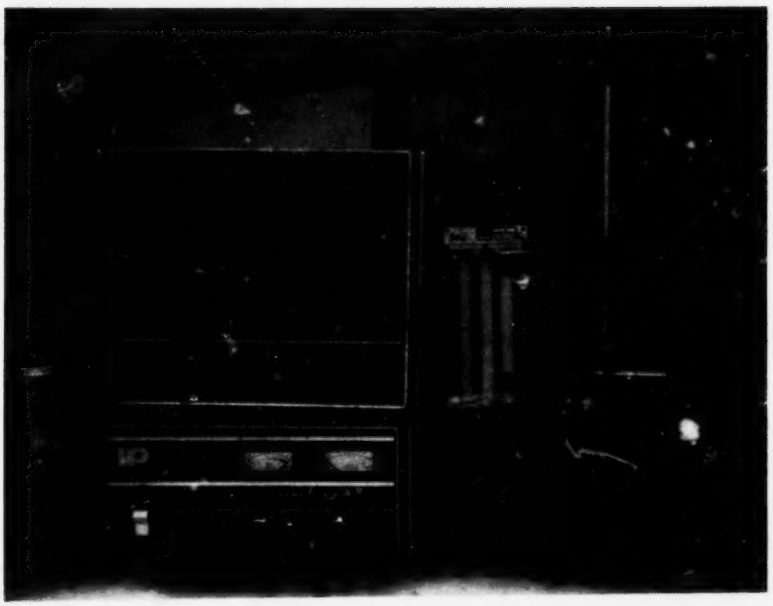

Figure 4. IPC Oxygen Research Plasma Instrument

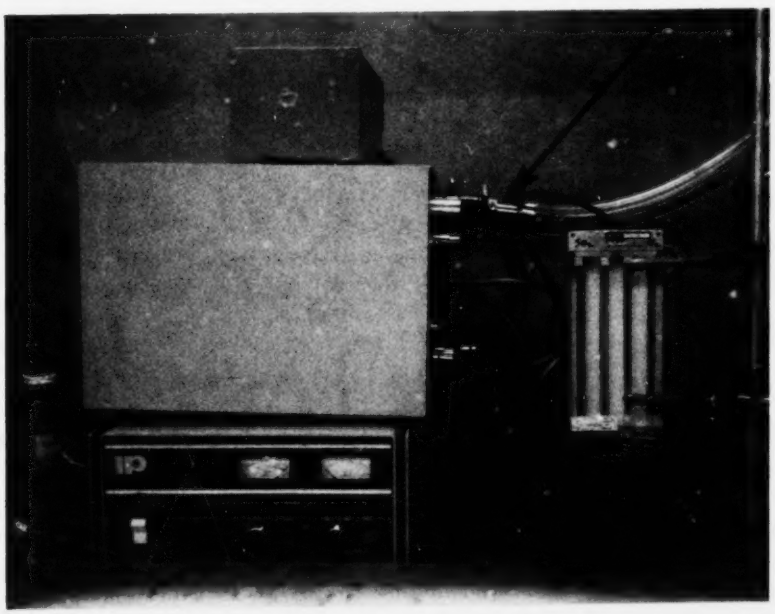

Figure 5. Experimental Arrangement for Evaluation of Solid Sorbents

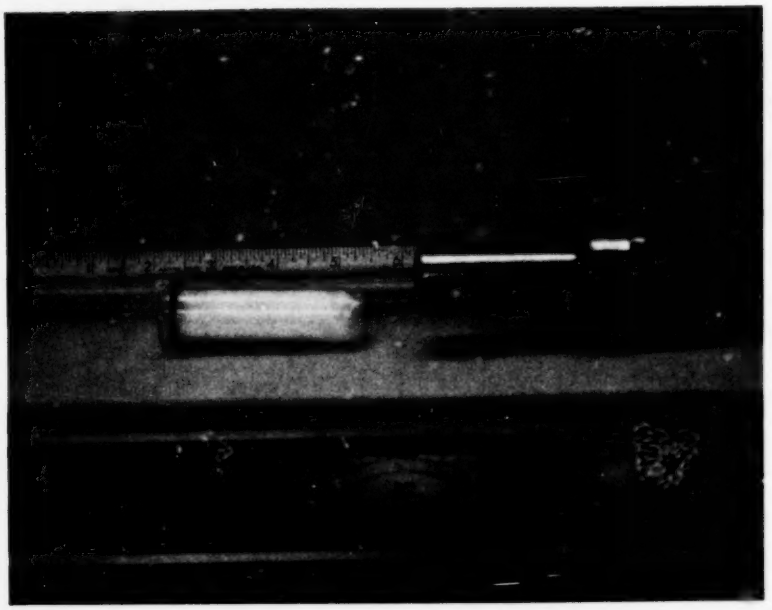

Figure 6. Solid Sorbent Canister

Figure 7. Solid Sorbent Canister Placed in Vacuum Line

the test, the pressure vessel was removed and excess SO_2 determined by titration with dilute base after sparging through a 3 percent H_2O_2 solution. The solid sorbent canisters were removed, extracted with an HCl/H_2O_2 solution and sulfur determined by precipitation as $BaSO_4$. In addition to the solid sorbents, the inside of the plasma asher reaction chambers was wiped as clean as possible with a dampened filter paper and residual sulfur determined by a $BaSO_4$ gravimetric analysis.

4.3.3 SO_x Sorbtion Studies — Results and Discussions

The results of the initial screening studies are shown in Table 13. Based on these studies, potassium permanganate and ammonium vanadate were chosen for further study under actual plasma conditions. Calcium oxide, sodium hydroxide and potassium hydroxide were also evaluated based on positive reports in the literature.[7,8] Linde molecular sieve 13X was used because of its ability to selectively absorb molecules less than 10Å in diameter ($SO_3 \approx 3$Å).[14] Because silica gel was used as a substrate, it was evaluated to establish a baseline.

Table 13. Atmospheric Absorption Studies

Compound	% Efficiency
Na_2CO_3	20
$NaHCO_3$	20
$KMnO_4$	110
NH_4VO_3	100
Silica Gel Neat	20

Besides the effects of varying sorbent concentrations, the effect of elevated temperature was also evaluated; chemisorption is a chemical reaction and will proceed more rapidly as the temperature is increased.[16] Because of the physical limitations of the experimental apparatus, 100°C was the maximum attainable temperature. Although this was probably not the optimum temperature for some of these systems, it was hoped that any trends to higher sulfur retention could be observed.

The results of 20 experimental runs are shown in Table 14. The percent recovery of sulfur based on SO_2 introduced was calculated by summing the amounts of sulfur species found in the reactor chamber and the sorbent. Of the sorbents tested, only $KMnO_4$ at 25°C and a 10:1 molar ratio and 30/50 mesh 13X mole sieve at 25°C yielded quantitative recovery. Adding caustic or heat did not increase recovery for the $KMnO_4$ system. Mole sieve exhibited increased sulfur sorption with a decrease in mesh size which is indicative of a surface area dependency.

KOH, NaOH, CaO, and NH_4VO_3 all showed increased sorption with elevation of temperature. In all the experiments, 17 to 41 percent of the added SO_2 was found retained within the reactor chamber of the plasma asher. Because of the physical configuration of the instrument, not all of the internal surfaces could be cleaned; therefore, the reported total values could be low by an unknown and possibly varying amount. The sorption of SO_x species on the chamber walls was unexpected and the mechanism is unexplained at this time. It is felt that the problem can be circumvented. Using a different reactor design in smaller removable chambers (for ease of cleaning) and placing the sorbent canisters either within or directly behind the reactor chambers would eliminate sorption sites which cannot be cleaned without completely dismantling the instrument. As redesign and fabrication were outside the scope of the task, further experimentation was discontinued.

Table 14. Evaluation of Solid Sorbents for SO_x Sorption Under Plasma Conditions

Sorbent System (mM)				% Recovery		
Test Number	Temperature	$KMnO_4$	KOH	Reactor Chamber	Sorbent	Total
1	25°C	-	13	30	15	45
2	25°C	12	-	13	32	45
3	25°C	6	6	41	14	55
4	25°C	6	-	23	67	90
5	25°C	-	26	23	40	63
6	100°C	4	4	13	21	34
7	100°C	4	-	24	23	47
8	100°C	10	-	28	20	48
9	100°C	-	9	17	23	40
10	25°C	13X mole sieve 16/30 mesh		21	42	63
11	25°C	13X mole sieve 30/50 mesh		17	71	88
12	25°C	13X mole sieve 30/50 mesh rerun		21	87	108

Table 14. Evaluation of Solid Sorbent for SO_x Sorption Under Plasma Conditions (continued)

Sorbent System mM						% Recovery		
Test Number	Temperature ^{0}C	$KMnO_4$	NaOH	NH_4VO_3	CaO	Reactor Chamber	Sorbent	Total
13	25	6	10	-	-	34	10	44
14	25	3	10	-	--	37	14	51
15	25	-	-	-	148	36	18	54
16	100	-	-	-	167	23	39	62
17	25	-	10	-	-	33	15	48
18	25	-	-	5	-	20	6	26
19	100	-	-	5	-	41	18	59
20	25	Activated Silica Gel Double Trap 40/80 mesh				36*	15*	51*

*Total of both traps

5. PROCEDURES FOR COAL SULFUR FORMS ANALYSIS VIA OXYGEN PLASMA ASHING

5.1 INTRODUCTION

The following methods present the laboratory analysis of coal for sulfur forms using a low temperature oxygen plasma. The basis of the analytical procedure is the selective removal, under plasma conditions, of the organic coal matrix including the organic sulfur species. This is accomplished with the unaltered retention of all inorganic sulfur compounds. The unaltered ash is either sequentially extracted with HCl and HNO_3 for sulfate and pyritic sulfur speciation, or extracted with HNO_3 to obtain the total inorganic sulfur. Total sulfur is determined by the highly accurate $BaSO_4$ gravimetric analysis of the nitric acid extract. These values are used in conjunction with an Eschka total sulfur analysis to calculate the organic sulfur content of the coal.

Analytical procedures appear in the order listed below. The standard ASTM procedures, when followed, are referenced. Reagent blanks must be obtained in all procedures.

5.2 Plasma ashing procedure

5.3 Inorganic sulfur procedures

a) Sulfate sulfur, ASTM D2492
b) Pyritic sulfur

5.4 Total inorganic sulfur

5.5 Total sulfur - Eschka ASTM D271

5.6 Moisture, ASTM D271

5.2 PLASMA ASHING PROCEDURE

Coal ground to 60 mesh x 0 or finer is ashed at low temperature in an oxygen plasma instrument.

5.2.1 Equipment

- Oxygen Plasma Asher - International Plasma Corporation Model 104B or equivalent.
- Balance capable of weighing to ±0.1 mg
- Petri dishes approximately 55 mm in diameter

5.2.2 Procedure

Weigh 1g of coal into a clean tared petri dish and place it in the reactor chamber of the plasma asher. Secure the chamber doors and initiate vacuum (Note 1). Adjust the input power to 100 watts and the oxygen flow to 200 cc/min. Interrupt the ashing at least once per day; remove and gently shake the sample to expose fresh surfaces (Note 1). The ashing is complete when a visual examination of the sample reveals the absence of black coal particles. This takes approximately 72 hours. At the termination of ashing, remove the samples and store in a clean, covered, draft-free area prior to analysis.

5.3 INORGANIC SULFUR FORMS

The following methods cover the determination of sulfate sulfur and pyritic sulfur in the plasma ash generated using the procedure in Section 5.2. A sequential extraction procedure patterned after ASTM D2492 is used. Sulfate sulfur in the HCl extract is determined as $BaSO_4$; pyritic sulfur extracted by the nitric acid is determined by atomic absorption analysis of pyritic iron (Note 2).

5.3.1 Procedure

Quantitatively transfer the plasma ashed sample into a 250 ml beaker with successive rinsings of 2/3 HCl; adjust acid volume to approximately 50 ml; boil for 1/2 hour and filter through Whatman #40 filter paper. Determine sulfate sulfur gravimetrically on the filtrate as per ASTM D2492. The residue to used for pyritic sulfur analysis.

Note 1. Initiation of vacuum or readjustment to atmospheric pressure should be performed slowly so as not to disturb the coal or coal ash. Rapid removal or introduction of air can blow samples out of the petri dishes.

Note 2. Sulfide sulfur, if present in the coal, will not be determined when this acid sequence is followed. An approximation of the sulfide concentration can be made by subtracting the total of the sulfate and pyritic sulfur from the total inorganic sulfur determined in Section 5.4.

5.3.2 Pyritic Sulfur

Pyritic sulfur is determined by an atomic absorption iron analysis performed on a nitric acid extract of the residue from the sulfate sulfur determination. Analysis is performed at a less sensitive iron line at 344.0 nm, using a bracketing technique with iron standards.

5.3.2.1 Equipment

- Atomic absorption spectrophotometer: Use iron lamp, set analytical wavelength at 344.0 nm with a slit width of 2 Å. Determination made using air-acetylene flame.
- Volumetrics: 250 ml
- Beakers: 250 ml with covers

5.3.2.2 Reagents

- Nitric acid (1/7): Mix 1 volume of concentrated nitric acid with 7 volumes of water.
- Atomic absorption iron standards: Prepare standards from 10 to 150 ppm in increments of 10 ppm by serial dilution of a 1000 ppm standard iron solution. Dilute standards with a 1/1 mixture of 1/7 HNO_3 and water.

5.3.2.3 Procedure

Transfer the filter paper and residue from the sulfate sulfur extraction to a 250 ml beaker. Add 50 ml 1/7 HNO_3, cover with a watch glass, and boil for 1/2 hour. Cool and filter through Whatman #40 filter paper directly into a 250 ml volumetric flask. Wash thoroughly with 1/7 HNO_3 and dilute to volume.

Adjust the atomic absorption spectrophotometer using the manufacturers directions, the 344.0 nm iron line, a 2 Å slit width, and an air-acetylene flame. Aspirate the sample in order to determine the approximate concentration. Bracket this concentration with iron standards and rerun sample; record five sample values taken over a 1-minute period of time.

5.4 TOTAL INORGANIC SULFUR

The total inorganic sulfur value is obtained by a $BaSO_4$ gravimetric analysis of a single nitric acid extraction of the plasma ashed sample. All inorganic sulfur compounds, including iron sulfide (FeS), are converted to sulfate and are reported as total inorganic sulfur.

5.4.1 Equipment

- pH meter and electrodes
- Beakers, 250 ml with covers
- Gooch crucibles: Prepare with an asbestos mat by filtering a water suspension of medium texture asbestos fiber. Wash with approximately 300 ml of hot water, ignite the crucible and mat at 900°C for 2 hours, remove, cool and weigh.

5.4.2 Reagents

- Nitric acid (1/7): Mix 1 volume of concentrated nitric acid with 7 volumes water
- $BaCl_2$ solution (100g/l): Dissolve 100g barium chloride in water and dilute to liter
- Filter aid: Water suspension of ash free paper pulp
- Ammonium hydroxide solution (1/1): Dilute concentrated ammonium hydroxide with equal volume of water.

5.4.3 Procedure

Quantitatively transfer the plasma ashed sample into a 250 ml beaker with successive washings of 1/7 nitric acid. Adjust the acid volume to approximately 50 ml; cover the beaker and boil for 1/2 hour. Filter the undissolved ash through a Whatman #40 filter paper into a 400 ml beaker. Wash the solids several times with 1/7 HNO_3. Adjust the pH of the filtrate to 1.1 ±0.1 using a pH meter and 1/1 NH_4OH. Bring the volume to approximately 300 ml with deionized water and heat to boiling. Add 10 ml of 10% $BaCl_2$ solution, cover and boil for an additional 1/2 hour. Remove the beakers and allow the $BaSO_4$ precipitate to sit overnight. Add a small amount of filter aid to the prepared Gooch crucibles and filter the precipitate. Wash it with approximately 200 ml of hot water, then ignite at 900°C for 2 hours. Cool and weigh.

5.5 TOTAL SULFUR

Perform Eschka analysis of separate whole coal sample using ASTM Method D271.

5.6 MOISTURE

Determine moisture content of whole coal using Method ASTM D271.

5.7 CALCULATIONS

5.7.1 Sulfate Sulfur

Calculate the percentage of sulfate sulfur as follows:

$$[(A-B) \times 13.74]/W = \text{Sulfate Sulfur \%}$$

where

A = grams of $BaSO_4$ precipitated

B = grams of $BaSO_4$ in the blank

W = grams of sample used

5.7.2 Pyritic Sulfur - Atomic Absorption

Calculate the percentage of pyritic sulfur as follows:

$$\frac{C \times D}{W \times 10^4} \times 1.148 = \text{pyritic sulfur \%}$$

where

C = iron concentration in ppm

D = solution volume

W = sample weight in grams

5.7.3 Organic Sulfur

Organic sulfur is calculated as the differences between as Eschka total sulfur and the total inorganic sulfur obtained on a plasma ashed sample. Calculate as follows:

$$\text{Organic Sulfur} = \frac{(A-B) \times 13.74}{W_1} - \frac{(C-D) \times 13.74}{W_2}$$

where

A = weight of $BaSO_4$ obtained from Eschka analysis in grams

B = weight of blank from Eschka analysis

W_1 = weight of sample used for Eschka analysis

C = weight of $BaSO_4$ obtained from total inorganic sulfur analysis

D = weight of blank from total inorganic analysis

W_2 = weight of sample taken for total inorganic sulfur analysis

5.7.4 Moisture

To calculate all results to a dry basis, multiply each result by

$$\frac{100}{(100 - \% \text{ moisture in sample})}$$

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APPENDIX A

LITERATURE SEARCH
COAL SULFUR ANALYSIS

A.1 INTRODUCTION

The following section contains a compilation of the literature concerning the analysis of coal for both total sulfur and sulfur forms. Included with the various sections are the unpublished results of several comparative analyses performed at TRW in conjunction with EPA contracts dealing with the Meyers Process (coal desulfurization via ferric sulfate leaching). Most of these experiments were designed to answer specific questions arising from the laboratory and bench scale development of this process which could not be answered using standard ASTM analytical procedures.

Of special interest is a review dealing with the evaluation of the U.S. Bureau of Mines Nuclear Sulfur Meter. This technique is given special emphasis as it offers promise for an on-line analytical procedure for total sulfur, moisture, ash and Btu measurement which has potentially wide application in coal cleaning facilities.

A.2 TOTAL SULFUR ANALYSIS

There are four ASTM procedures for the determination of total sulfur in coal. These are Eschka, bomb combustion, high temperature combustion (Leco) and peroxide combustion procedures. All four involve the conversion of sulfur to its oxides and quantification either by precipitation as $BaSO_4$ or titration by base after conversion to acid (high temperature combustion). Several modifications of the basic procedures have been tried. The modifications involve a change in the final determination of sulfate and include volumetric determinations in the Eschka and bomb combustion methods and an infrared detection system for the high temperature combustion procedure.

Additional procedures used for total sulfur analysis include oxygen flask combustion followed by either titration or a flame photometric detection of the sulfur oxides and nondestructive techniques including X-ray fluorescence and a gamma ray emission nuclear sulfur meter. Of these procedures only X-ray fluorescence has been used to any extent for quantitative laboratory analysis.

A.2.1 Eschka Procedure - ASTM D271

The Eschka[1] procedure has been used for routine accurate analysis of coal for approximately 100 years and is accepted as a national standard in several countries.[17] The procedure involves the controlled combustion of coal in a mixture of 1 part sodium carbonate and 2 parts of light calcined magnesium carbonate. The sulfur compounds evolved during combustion react with the sodium carbonate and under the oxidizing conditions employed are retained as sodium sulfate. Sulfate is quantitated by precipitation of sulfate after work-up of the Eschka mixture. When performed by a competent analyst, the Eschka procedure is accurate and precise. A slight negative bias when very high sulfur coals are analyzed has been reported in the literature[18] and has been confirmed by our laboratory using Meyers processed coal samples doped with elemental sulfur. Table A-1 shows the results of experiments which compared the three most common ASTM procedures. Note that the bomb combustion procedure showed the highest recovery. The slightly lower recovery of the Leco and Eschka procedures could be the result of a smaller amount of sulfur being volatilized before conversion to sulfur oxides.

A.2.2 Eschka Procedure - Volumetric Finish

In order to circumvent the time needed to complete an accurate gravimetric sulfate analysis, several volumetric procedures for the determination of sulfate have been proposed.[19,20] These involve the direct titration of sulfate using either barium chloride or barium perchlorate and a variety of end point indicators. These methods generally lacked a distinct end point; however, arsenazo III has given a much more distinct end point than even the commonly used thorin.[19,20] These techniques have been applied to the hot water extract from the Eschka fusion product,[19] as well as to an oxygen flask procedure,[20] with excellent results. If the conditions are properly controlled, the accuracy and precision of these methods are close to the gravimetric portion of the Eschka procedure. Interference from cations is both common and serious and hinders sulfate precipitations and/or causes precipitation of the indicator. As a result, cations should be removed with an ion exchange column prior to analysis. This step is time-consuming, thereby nullifying the significant labor savings inherent in these methods.

Table A-1. Total Sulfur Analysis of High Sulfur Coals

Sample Doped With Elemental Sulfur	Bomb Wash		Leco		Eschka		%Recovery		
	Calculated Sulfur	Analyzed Sulfur	Calculated Sulfur	Analyzed Sulfur	Calculated Sulfur	Analyzed Sulfur	Bomb Wash	Leco	Eschka
ROM Coal	6.96	6.83	6.80	6.53 ±0.10	7.15	6.96 ±0.03	98	96	97
Hexane Refluxed	6.97	6.82	6.73	6.44 ±0.001	7.16	6.77	98	96	95
Heptane Refluxed	7.20	7.20	7.09	6.70 ±0.01	7.39	7.10 ±0.06	100	94	96
Toluene Refluxed	7.16	7.11	6.83	6.74 ±0.00	7.35	7.00	99	99	95

A.2.3 Bomb Combustion - Gravimetric Finish ASTM-D271, D3177[1,21]

In this procedure, approximately 1g of coal is combusted in a stainless steel Parr bomb containing 30 atm. oxygen and a small volume of water or dilute sodium carbonate to dissolve the sulfur oxides. After the removal of iron as the hydroxide, the pH is adjusted and sulfur is determined as $BaSO_4$.

At TRW it has been found that the bomb wash procedure using the gravimetric finish is equally or more precise than the Eschka procedure. However, some analysts[16] have reported retention of sulfur in the fused ash and an additional extraction step was necessary for accurate analysis. The gravimetric portion of this procedure is subject to interference from iron. Unless carefully removed, the iron will yield low sulfur values because it can be occluded as iron sulfate in the $BaSO_4$ precipitate and can be converted to ferric oxide during the ignition step. Additional care must be taken to avoid occlusion of sulfate when the iron is precipitated. If large volumes of ferric hydroxide are precipitated, it is mandatory to redissolve and reprecipitate to obtain a quantitative recovery of sulfate.

A.2.4 Bomb Combustion - Volumetric Finish

Only one volumetric technique has been evaluated as a finishing technique for the bomb combustion procedure. This is a potentiometric titration procedure using a lead perchlorate titrant and a lead ion-selective electrode.[22] This procedure has been claimed to be more rapid and precise than the standard gravimetric technique. However, significant interferences are noted from copper, mercury and silver with the electrode, and nitrate, chloride and bicarbonate with the titrant.
Phosphate must also be absent. In view of these interferences and the fact that nitrogen, carbonate, phosphate, and chloride can be major constituents of coal or coal ash, it is difficult to see that this technique can be applied to a wide variety of coals with dependable accuracy and precision.

A.2.5 High Temperature Combustion - Titration ASTM D3177-75[22]

This procedure entails the controlled combustion of the coal sample in a specially designed furnace. Combustion products including SO_2 are swept out of the reaction zone into a H_2O_2 trap where the resulting sulfuric acid is titrated with dilute base. This technique is less precise

but much faster than the Eschka or Parr bomb methods. Typically seven or eight analyses can be completed per hour. Chlorine is a positive interferent but a correction can be made by back titrating the NaOH liberated by the reaction of chloride with mercuric oxycyanide. This reaction can also be used to determine the chlorine content of the coal.

A.2.6 High Temperature Combustion - Infrared Detection of Sulfur[20]

A new instrument is being marketed by Leco Corporation for the rapid determination of sulfur in coal and coke. This instrument is based on the combustion of ~0.5g of coal in an induction furnace swept with oxygen. The SO_2 combustion products are selectively measured by an infrared detector. All sulfur compounds are completely decomposed during the high temperature combustion and a heated delivery system prevents loss of SO_2 between the furnace and the detector. The manufacturer claims an accuracy of ±3%; however, communications with users indicate that ±5% is probably more realistic.

A.2.7 Peroxide Bomb - ASTM D271[1]

Although precision and accuracy of this method are reportedly equivalent to the Eschka procedure, this procedure is seldom used.

A.2.8 X-Ray Fluorescence[24, 29]

Of the non-ASTM procedures, the X-ray fluorescence technique is probably the most widely used. This technique is based on the detection and quantitation of sulfur Kα or Kβ X-ray emissions. When the proper sample preparation steps are employed and corrections made for interferences from Ca, Mg, Al, Si and Fe, the precision is equal to that of standard ASTM procedures. The major difficulty in obtaining an accurate analysis is in preparing the samples because the sulfur fluorescence yield increases greatly as the average particle size of the sample decreases.[24,26] For optimum analysis, samples are ground to pass through a 325 mesh screen prior to pelletizing and analyzing. When performed properly, this technique reduces analysis time and can be used to quantitate other elements.

Variations in relative intensities of the S Kα and Kβ lines have been noted by Berman[28] in calibration curves developed by comparing doped mineral matter free coal with high pyrite content coal. The variations

were attributed to a shift of the Kβ line caused by differences in sulfur bonding. The bonding shift is the basis of a "soft X-ray" procedure which has been used to directly determine the forms of sulfur in coal.[29] With this procedure four X-ray intensity measurements are taken of the S, Kα and β lines and the sulfur forms are calculated. A comparison of this method with the ASTM results showed good agreement.[29] However, when large amounts of several forms of sulfur are present, tests by EPA have shown that it is very difficult to obtain enough resolution for a precise and accurate sulfur forms analysis.

A.3 U.S. BUREAU OF MINES NUCLEAR SULFUR METER[30, 32]

This analytical system is based on prompt monitoring of gamma rays produced by the interaction of fast neutrons with coal. In this method, fast neutrons are emitted equally in all directions from a small capsule of californium-252 centered in a bin of coal. The neutrons penetrate the coal and are slowed by multiple collisions which produce a sphere of thermal neutrons that are captured by the elements in coal, in proportion to their neutron cross sections. These neutron capture reactions produce prompt gamma rays with energies characteristic of each element. A gamma ray detector then records the gamma ray spectrum. Sulfur atoms in coal, for example, produce 5.4-MeV gamma rays which appear in a gamma ray spectrum as a peak whose height is directly proportional to the sulfur content of the solid fuel. The detector is a 6- by 7-inch sodium iodide crystal that provides a reasonable compromise between detection efficiency, resolution, activation, and cost.

Californium-252 was chosen for the analysis of coal because it emits low-energy neutrons that do not cause appreciable interference from inelastic neutron scattering reactions. The amount of californium-252 required for sulfur measurement in coal depends on the required measurement response time. An 80-100 microgram source provides a 2-minute response time without necessitating source replacement for several years. (The half-life of californium-252 is 2.6 years.) The material being measured is not rendered radioactive. This method is discussed in two major papers[30,31] which review several years of research and development. The first discusses a bench scale development effort which resulted in a "hard wired" system ready for installation and checkout at a commercial coal cleaning facility. The

second paper discusses checkout activities and actual use of the instrument in the field.

The main advantage of this system is that it is truly an on-line system. The analyses are performed within minutes on a moving stream of 1/4" x 0 coal with each data point representing the analysis of 300 to 800 pounds of coal. This eliminates one of the major problems associated with coal analysis which is the technique and effort involved in obtaining a representative 2g sample from very large quantities of coal. With the use of additional channels, the system could also be used to measure ash, moisture and heat content, simultaneously, although no attempt was made to actually perform these analyses. In a carefully calibrated system, precision was found to be ±0.02% and accuracy to be ±0.05%. These values are well with the ASTM D271 guidelines of 0.2% reproducibility and 0.1% repeatability.

A major disadvantage in using such an expensive instrument is that there is no universal agreement that continuous monitoring will facilitate an increase in productivity of a coal cleaning plant. Also the detector system appears to be similar to those used for energy dispersive X-rays. Problems associated with both systems include poor resolution of the sulfur escape peak from peaks associated with other elements. Poor resolution is compensated for by the use of additional channels in the detector electronics and a computer to subtract background interferences from the sulfur signal. At times the background is substantial and reduces the precision and accuracy of the measurement. Two channels must be used for sulfur monitoring so that, when the number of pulses overloads the first channel, the pulses can be collected in the second. This results in better resolution and a correspondingly higher degree of accuracy and precision at high levels of sulfur. However, because of the nature of counting statistics, it is expected that the accuracy and precision of the system will deteriorate. Although it is not explicitly stated in these papers, it appears that instrumental adjustments must be empirically set in the field to eliminate interferences from moisture, iron and ash constituents.

Another disadvantage of this system is that it must be calibrated in the field by comparing instrument response to chemical analysis of the corresponding samples. Removal and reinsertion of the neutron source substantially alters these calibrations. In addition, the data presented in the papers indicate fluctuations of 0.2-0.4% which varies substantially with the claimed precision of ±0.02%. The reason given for these fluctuations is nonuniform coal flow[24] which conflicts with claims that the system is relatively unresponsive to bulk density and flow rate.[30] The fluctuations could become more pronounced when using larger counting periods for coals that are low in sulfur. This is a serious disadvantage because accuracy and precision must be increased as the total sulfur content of the coal reaches the low levels required by coking coal or air pollution control requirements.

Additional evaluation of this instrumental system should be performed using lower sulfur coal (~1.0 percent) and varying quantities of iron oxide, ash constituents and moisture. These parameters should be evaluated at one instrument setting for varying coal flow rates and counting periods. As the system is by design a process monitoring technique for coal cleaning facilities, it should be proven to be unresponsive to possible variations in coal ash, iron and water content.

A.4 SULFUR FORMS ANALYSIS

Sulfur forms analysis involves the determination of sulfate, pyritic and organic sulfur. Although other techniques have been investigated, ASTM Method D2492 is used almost exclusively. The ASTM method involves the selective extraction and determination of sulfate and pyritic sulfur; these values are subtracted from the total sulfur to determine (or estimate) the organic sulfur. After extraction, several variations on the ASTM procedures have been attempted with varying degrees of success. Only the Illinois Geological Survey has developed a unique reductive technique for the determination of sulfur forms. In addition to the chemical methods, several X-ray methods have been developed for the determination of total sulfur and/or sulfur forms directly on the coal. These methods, along with TRW's oxygen plasma technique are discussed in the following sections.

A.4.1 Sulfate Sulfur - ASTM Method[1]

ASTM method D2492 for sulfate sulfur involves a 30 minute hot 8N HCl extraction of coal and gravimetric determination of sulfate in the extract. Dilute HCl solutions have been shown to attack pyrite upon standing at room temperature.[22] This problem is attributed to reaction with dissolved oxygen which is more soluble in dilute than in concentrated HCl solutions. The ASTM procedure avoids this problem by using hot (boiling) HCl and limiting contact to 30 minutes. Variations of this basic analytical scheme substitute either titrimetric[33] or turbidimetric[2] procedures for the sulfate determination. Limited success was achieved because interferences from materials extracted from the coal ash required clean-up procedures that increased the analysis time to nearly that of the ASTM analysis discussed below. A direct analysis using the soft X-ray approach (cf. Section A.2.8) has also been used with very limited success. Other modifications have been investigated in an attempt to increase the sensitivity and reduce the time to perform the analysis. The ASTM $BaSO_4$ gravimetric determination, however, remains the method of choice.

A.4.2 Sulfate Sulfur - Titrimetric[33]

The procedure described entails the redissolution of precipitated $BaSO_4$ in an alkaline EDTA solution and a back titration of excess EDTA with a standardized magnesium chloride solution using Eriochrome Black T as an indicator. Results compared favorably with gravimetric checks. Better sensitivity was found but no indication of precision or interferences was reported.

A.4.3 Sulfate Sulfur - Turbidimetric[2]

The ASTM $BaSO_4$ gravimetric procedure, as described above, is relatively long and complicated. In order to avoid this, experiments were performed at TRW to adapt standard turbidimetric procedures to this analysis. In all cases, the results of this method were compared to ASTM results on the same solution. It was found that this method is very sensitive to extraction conditions and tends to give distinctly low results unless cations (probably iron) are removed before analysis. The experimental matrix, showing the effect of digestion time, type of oxidizing agent, and the removal of cations by ion exchange resin, is shown in Table A-2. The need to remove

Table A-2. Sulfate Analysis Comparison

Sample	Digestion (Reflux) Time, Hours	Sulfate Sulfur, Wt. %		
			Turbidimetric	
			Peroxide	Bromine
		ASTM[a]	oxidant[a]	oxidant[a]
ROM (Weathered) L.K. Coal	0.5	0.61 ±0.03		
	1	0.62 ±0.01	0.14 ±0.03	0.15 ±0.02
	2	0.64 ±0.01	0.18 ±0.05	0.14 ±0.05
	3	0.67 ±0.01	0.24 ±0.08	0.24 ±0.01
Meyers Processed Coal #1	0.5	0.29 ±0.02	0.16 ±0.01	
	1	0.31 ±0.01	<0.01	<0.01
	2	0.35 ±0.01	0.16 ±0.01	0.19 ±0.02
	3	0.39 ±0.02	0.04 ±0.01	0.04
Meyers Processed Coal #2	0.5	0.60	0.27 ±0.00	
	1	0.63 ±0.01	0.24 ±0.02	0.27 ±0.04
	2	0.64 ±0.00	0.30 ±0.03	0.28 ±0.01
	3	0.65 ±0.01	0.19 ±0.02	0.31 ±0.04
Processed Coal Doped with Ferric Sulfate	1	(0.60)[b], 0.61	0.41, 0.61[c]	-
	2	(0.60)[b], 0.62	0.33, 0.67	-
	3	(0.60)[b], 0.62	0.37, 0.61	-

(a) All analysis performed in triplicate
(b) Calculated sulfate value of sample (ASTM determined sulfate sulfur value and added ferric sulfate
(c) Cation-exchanged turbidimetric analysis values

cations before final analysis increases the time and labor to the point where the ASTM procedure is still preferred.

A.4.4 Pyritic Sulfur - ASTM Method[1]

This procedure was first recommended by Powell in 1919 and still remains the method of choice.[24] Pyritic sulfur is extracted from coal by the oxidative attack of boiling dilute nitric acid. Because varying amounts of organic sulfur are also extracted, pyritic sulfur is quantified by the determination of pyritic iron. Therefore, removal of non-pyritic iron is necessary either directly or as a blank with HCl. This correction or pre-extraction is performed in the sulfate extractions step. In the ASTM procedure, the pyritic iron is titrated directly with either dichromate or permanganate solution. This procedure is long and involved because of the need to first destroy any organic compounds that have been extracted. In spite of these precautions, organics often remain, causing indistinct and fading end points. In addition, very fine (<5μ) occluded pyritic sulfur often is not extracted. The reproducibility between operators also is often surprisingly different for certain coals. For this reason ASTM has set the reproducibility for duplicate determinations carried out by different laboratories to be 0.3% and 0.4% for coals having less than and greater than 2% pyritic sulfur, respectively. These limits are often not satisfactory for modern coal cleaning engineering calculations.

A.4.5 Pyritic Sulfur - ASTM Extraction - Determination of Iron by Atomic Absorption

In order to overcome the problems inherent in the ASTM procedure for work on the TRW-EPA Meyers Process, an atomic absorption procedure was developed to replace the ASTM titrimetric procedure.[2] This technique eliminates the complex work-up and the interferences associated with the titration procedure by using the specific iron absorption at 344.0 nm. Absorption readings are taken using a short curve approach which increases the normal AA precision. Table A-3 lists a series of comparison analyses made on 46 samples where the pyritic sulfur ranged from less than 0.1% to greater than 5.0%.

Table A-3. Pyritic Sulfur Analysis[a],[b],[c] Atomic Absorption (AAS) vs. ASTM Procedures

Coal Mine Sample	% w/w Pyritic Sulfur		Sample	% w/w Pyritic Sulfur	
	AAS	ASTM		AAS	ASTM
Muskingum	0.22 ±0.028	0.26 ±0.007	Marion	0.06 ±0.021	0.05 ±0.022
Powhattan No. 4	0.46 ±0.064	0.43 ±0.057	Mathies	0.02 ±0.000	0.08 ±0.000
Isabella	0.06 ±0.007	0.07 ±0.007	Meigs	0.18 ±0.035	0.16 ±0.035
Mathies	0.08 ±0.000	0.02 ±0.000	Powhattan	0.46 ±0.064	-
Williams	0.28 ±0.049	0.30 ±0.035	Eagle No. 2	0.18	0.11
Robinson Run	0.08 ±0.014	0.08 ±0.014	Jane	0.62	0.63
Shoemaker	0.44 ±0.148	0.46 ±0.120	Fox	0.50	0.47
Delmont	0.22 ±0.078	0.20 ±0.134	Meigs[e]	0.43	0.43
Marion	0.04 ±0.007	0.05 ±0.014	Powhattan No. 4[e]	0.64	0.54
Lucas	0.22 ±0.049	0.20 ±0.007	Muskingum[e]	0.60	0.48
Bird No. 3	0.11 ±0.014	0.16 ±0.035	Mathies[c]	0.98 ±0.007	1.05 ±0.065
Martinka	0.12 ±0.007	0.12 ±0.007	Marion	0.84 ±0.007	0.90 ±0.017
Meigs	0.18 ±0.035	0.16 ±0.035	Powhattan No. 4	2.53 ±0.000	2.57 ±0.060
Dean	0.20 ±0.007	0.16 ±0.035	Robinson Run	2.72 ±0.014	2.89 ±0.190
Kopperston No. 2	0.02 ±0.000	0.06 ±0.035	Lucas	1.24 ±0.007	1.42 ±0.082
Harris No. 1 and 2	0.02 ±0.000	0.07 ±0.042	Williams	1.94 ±0.000	2.23 ±0.062
North River	0.17 ±0.028	0.12 ±0.021	Isabella	1.05 ±0.042	1.07 ±0.070
Homestead	0.22 ±0.028	0.22 ±0.092	Shoemaker	2.18 ±0.007	2.19 ±0.100
Ken	0.24 ±0.050	0.30 ±0.050	Meigs	1.88 ±0.191	2.19 ±0.030
Star	0.04 ±0.021	0.08 ±0.028	Bird No. 3	2.64 ±0.021	2.87 ±0.062
Eagle No. 2	0.25 ±0.004[d]	0.19	Delmont	4.27 ±0.014	4.56 ±0.044
Lower Kittanning	0.48 ±0.038[d]	0.33 ±0.035	Eagle No. 2	2.66 ±0.03[d]	2.67 ±0.15[d]
Lucas	0.12 ±0.007	0.21 ±0.034	Egypt Valley	4.70 ±0.004[d]	5.07 ±0.02[d]

[a] Unless otherwise noted, all analysis have been performed on two samples of treated coal.

[b] Values without standard deviation are single determinations.

[c] All values greater than 1% are untreated coal.

[d] Average of 3 determinations.

[e] Analysis from trial runs.

Precision of the analysis was found to be better using the AA procedure as the pooled standard deviation is 0.032 for the AA and 0.060 for the ASTM procedure. Agreement between the two procedures is excellent with few outliers. There is currently an ASTM committee evaluating a similar AA procedure for pyritic iron and it is expected that this procedure will be adopted by the ASTM within a year.

A.4.6 Pyritic Sulfur - X-Ray Fluorescence[10,27,35]

In support of the Meyers Process bench scale coal desulfurization program, initial development and evaluation of an X-ray fluorescence determination of pyritic iron in coal was investigated.[35] The procedure as applied is similar to the total iron procedure used by the Illinois State Geological Survey.[10,27] In this procedure, nonpyritic iron is first extracted with dilute HCl, then the residue is dried, pelletized and analyzed by X-ray fluorescence spectroscopy using the Fe Kα line. The major problem with the procedure is the preparation of standards with which the analysis of coal can be made because the calibration curve must be generated using coal with known amounts of naturally occurring pyrite.* The problem is attributed to the presence of finely divided pyrite (1-15 microns) which increases the fluorescence yield. Reasonably accurate (based on ASTM comparative analysis) analysis of several coals were obtained when the above procedure was followed. The results are tabulated in Table A-4.

Experience at IGS has shown that the precision and accuracy of this type of procedure is usually best in the iron range of 1-3%.* Beyond 3%, the calibration curve has a tendency to become nonlinear and below 1%, the precision and accuracy suffers somewhat from matrix effects. Typical precision for a total iron analysis is 0.04 RSD for the X-ray procedure and 0.05 for the ASTM procedure.[27]

A.4.7 Pyritic Sulfur - X-Ray Diffraction[36]

Iron pyrite is a member of the cubic system which gives rise to strong, well defined X-ray diffraction lines. The monitoring of the 311 reflection and comparison to an internal standard reflection from Ni (200 line) is the basis of a computerized X-ray diffraction procedure developed by the U.S. Bureau of Mines. Sensitivity of X-ray diffraction is normally limited

*Personal communication, Dr. J. J. Kubn, Illinois State Geological Survey.

Table A-4. Pyritic Sulfur Analysis - ASTM Vs. X-Ray Fluorescence Procedures % w/w

Coal Mine	ASTM	X-Ray
Harris	0.66	0.98
Isabella	1.42	1.30
Lucas	1.43	1.58
Shoemaker	2.28	2.10
Bird	2.47	2.68
Delmont	3.94	3.94

to compounds present at 5% or greater. The Bureau of Mines procedure makes use of a scanning capability with instrumental output stored in a computer. The scan may be automatically repeated for any number of times with the results for each scan accumulated. Comparative analysis with ASTM values shows reasonable agreement. Standard deviation is approximately equal to that attainable from the ASTM procedure although the time of analysis is much shorter. High mineral matter coals give rise to background reflections which interfere with both the pyrite and nickel peaks. When this condition exists, the reproducibility of the analysis deteriorates.

A.4.8 Pyritic Sulfur - Reduction Technique Using Lithium Aluminum Hydride (LAH)[27]

The Illinois State Geological Survey (IGS) has developed a procedure for pyritic sulfur analysis based on the reaction of pyrite with lithium aluminum hydride in tetrahydrofuran which converts the pyrite (FeS_2) to iron sulfide (FeS). Subsequent acidification of the sulfide liberates H_2S which is trapped in a gas scrubber containing a $CdSO_4$ solution. Reaction of H_2S with $CdSO_4$ liberates H_2SO_4 which is then titrated with a standardized base. Pyritic sulfur values compare favorably with ASTM values. Precision is ±0.05 which is the same as values generated using the ASTM procedure. Problems encountered involving the mesh size are compensated for by grinding samples to 400 mesh x 0. The procedure is not readily adaptable to routine analysis as LAH is very hazardous to handle and must be kept away from moisture.

A.5 DIRECT DETERMINATION OF ORGANIC SULFUR

Experimentation to directly determine organic sulfur in coal was initiated by Powell and Parr in 1919; a series of solvents was used to solubilize the organic sulfur.[34] Although they found that phenol dissolved the largest amount of the coal organic matter, less than one-half of the organic sulfur was removed. In a different approach, inorganic sulfur was first removed by nitric acid extraction, then the residue was extracted with hot alkali. This extract contained what they termed humic acids; "humic" sulfur contained little ash and the major portion of organic sulfur (total sulfur less the pyritic and sulfate sulfur). Because of the variability and difficulty in obtaining exact balances, it was decided that humic sulfur could not be determined directly. Since this time, organic sulfur has been determined by subtraction of the pyritic and sulfate sulfur from the total sulfur. The major difficulty with this approach is that inaccuracies and lack of precision in the total, sulfate and pyritic sulfur determination are cumulative and result in lack of accuracy and precision in the calculated organic sulfur value. The pooled standard deviation for the several hundred samples analyzed for TRW's Meyers Process was ±0.1%.[2] It was also found, with coals containing significant amounts of finely divided pyritic sulfur, that the nitric acid extraction is often variable and incomplete; this resulted in significant differences (0.1-0.5%) in the determined organic sulfur when performed at different times or in different laboratories. Precision in a given set of analyses was usually within the above limits. To avoid these problems, several alternative procedures have recently been tested to determine organic sulfur directly. These approaches include a soft X-ray method, microprobe analysis, and an approach using oxygen plasma.

A.5.1 Organic Sulfur - Soft X-Ray Method[29]

This method was discussed in Section A.4. Accuracy and precision are in good agreement with ASTM values in selected coals where one form of sulfur predominates. However, serious resolution problems occur when several forms of sulfur are present in large amounts. In these cases, precision and accuracy degenerate rapidly and the results are of little use.

A.5.2 Organic Sulfur - Microprobe Analysis[37]

In this method, coal samples are pretreated with HCl to remove soluble iron and sulfate sulfur and then further cleaned by float-sink procedures at a specific gravity of 1.2. The resulting float fraction, which contains about 80% of the total organic sulfur, is dried, pelletized and a polished section is analyzed. This is accomplished by a scanning technique which analyzes at least 100 points for both iron and sulfur. The organic sulfur is calculated after a correction factor for unremoved pyrite is applied. Only one analysis was reported and the precision of analysis was ±0.13%. Presently, United Technologies Research Corporation is working on a technique to analyze both pyrite and organic sulfur without extensive preparation procedures.

A.5.3 Organic Sulfur - Oxygen Plasma

An oxygen plasma technique for the direct determination of organic sulfur is presently being investigated. This is the subject of Section 4 of this report and the reader is referred there for details.